

AD-A102 290

IBM RESEARCH LAB SAN JOSE CALIF

F/G 11/9

POLY(P-PHENYLENE SULFIDE) HEXAFLUOROARSENATE: A NOVEL CONDUCTIN--ETC(U)

JUL 81 T C CLARKE, K K KANAZAWA, V Y LEE

N00014-80-C-0779

UNCLASSIFIED

TR-1

NL

1 of 1  
AD-A102 290



END  
DATE  
FILMED  
8-81  
DTIC

AD A102290

LEVEL II

12

OFFICE OF NAVAL RESEARCH

Contract N00014-80-C-0779

Technical Report No. 1

Poly(p-Phenylene Sulfide) Hexafluoroarsenate:

A Novel Conducting Polymer .

by

T. C. Clarke, K. K. Kanazawa, V. Y. Lee,  
J. F. Rabolt, J. R. Reynolds, and G. B. Street

Prepared for Publication

in the

Journal of Polymer Science

Polymer Physics Edition

IBM Research Laboratory  
5600 Cottle Rd.  
San Jose, CA 95193

28 Jul 1981

Reproduction in whole or in part is permitted for  
any purpose of the United States Government

This Document has been approved for public release  
and sale; its distribution is unlimited

DTIC FILE COPY

401-1-1  
81-7-27-115

DTIC  
ELECTE  
S AUG 0 1981 D

12, 26

RJ2945 (36890) 9/22/80  
Chemistry

POLY(P-PHENYLENE SULFIDE) HEXAFLUOROARSENATE:  
A NOVEL CONDUCTING POLYMER

T. C. Clarke  
K. K. Kanazawa  
V. Y. Lee  
J. F. Rabolt  
J. R. Reynolds  
G. B. Street

IBM Research Laboratory  
San Jose, California 95193

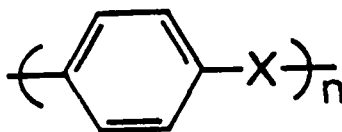
ABSTRACT: Poly(p-phenylene sulfide) (PPS) is a melt and solution processible polymer which on treatment with  $\text{AsF}_5$  forms a blue-black material with a conductivity of  $1-10 \text{ ohm}^{-1}\text{-cm}^{-1}$ . Thermopower measurements indicate that the resulting polymer is p-type, consistent with partial oxidation of the PPS by the  $\text{AsF}_5$ . The rate and extent of this doping process prove to be particularly sensitive to the degree of crystallinity of the starting polymer. There is no evidence of crosslinking of the polymer chains during the reaction with  $\text{AsF}_5$ . The details of both the chemistry and physics of the doping of PPS and several of its derivatives are presented.

Accession For	
NTIS GRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A	

## Introduction

Conjugated polymers have attracted significant attention over the past few years as they have been shown to display many of the properties normally associated with traditional metals and semiconductors.<sup>1</sup> Thus polythiazyl,  $(\text{SN})_x$ , was the first polymer found to undergo a superconducting transition.<sup>2</sup> Subsequently Chiang, et al.,<sup>3</sup> discovered that the electrical conductivity of polyacetylene,  $(\text{CH})_x$ , can be controllably varied over 12 orders of magnitude by the use of appropriate n- and p-type dopants. More recently polypyrrole<sup>4</sup> and poly(p-phenylene) (PPP)<sup>5</sup> have been shown to exhibit high conductivities in their oxidized forms. Actual application of these polymers has been limited, however, by their lack of ready processability. Thus  $(\text{SN})_x$  is only available in the form of relatively small crystals and supported films.  $(\text{CH})_x$  and polypyrrole are generated in the form of films which are not susceptible to further processing. PPP is a powder which is capable of limited processing by sintering prior to doping. None of these compounds in either their pristine or doped states achieve the ultimate goal of a material which combines the desired electrical properties with the attractive processing characteristics displayed by many synthetic polymers.

In our attempts to develop a more tractable conducting polymer system we have investigated a number of different polymer types. Perhaps the most interesting of these are the heteroatom linked polyphenylenes represented schematically by Structure I. In addition to providing the conjugated



I

backbone necessary for extended delocalization, these systems are expected to be more flexible than the parent poly(p-phenylene) and perhaps to display better processing characteristics. Two members

of this series are, in fact, well characterized polymers with excellent processing properties. Both poly(p-phenylene oxide) ( $X=O$ )<sup>6</sup> and poly(p-phenylene sulfide) ( $X=S$ )<sup>7</sup> are soluble polymers with well defined glass transition temperatures and melting points. We now find that poly(p-phenylene sulfide) (PPS) is also capable of being doped to high levels of conductivity using the strong electron acceptor arsenic pentafluoride. Presented below are the details of both the physics and chemistry of this doping process.<sup>8,9</sup>

### *Experimental*

All samples of PPS were used as received from Phillips Petroleum. The film and fiber materials were made available only in small experimental quantities and are not commercially available. Poly(m-phenylene sulfide),<sup>10,11</sup> poly(m,p-phenylene sulfide),<sup>10,11</sup> poly(p-phenylene oxide),<sup>6,12</sup> and poly(tetrafluoro-p-phenylene sulfide)<sup>13</sup> were prepared by literature procedures. Poly(2,6-dimethyl-p-phenylene oxide) was purchased from Aldrich. Arsenic pentafluoride was purchased from ROC/RIC and purified before use. For purification the  $AsF_5$  was first condensed in a 316 stainless steel container at liquid nitrogen temperature. While at  $-196^\circ C$  the sample was pumped to remove non-condensable impurities. The sample was then warmed to  $-131^\circ C$  and again pumped to remove volatile impurities in the  $AsF_5$  which have been identified by IR as  $SiF_4$  and  $CF_4$ . After warming to room temperature the sample was again cooled to  $-131^\circ C$  and pumped. This cycle was repeated until the vapor pressure of the sample at  $-131^\circ C$  was approximately 0.12 Torr as expected for pure  $AsF_5$ .<sup>14</sup> Mass spectroscopic investigation of  $AsF_5$  samples prepared in this fashion showed no detectable impurities. In particular  $AsF_5$  so treated was found to be free of  $AsF_3$  and HF.

All doping experiments were carried out in a 316 stainless steel vacuum system. Pressure in the system was monitored directly using either an MKS Baratron capacitance manometer (.001 to 10 Torr) or a Helicoid gauge designed for use with fluorine (1 to 760 Torr). The actual doping vessel was a 300 cc 316 stainless steel Parr bomb. In a typical experiment a pre-weighed PPS sample was placed in the Parr bomb which was then evacuated. A specific pressure of  $AsF_5$  was introduced and the bomb was sealed for the desired length of time, after which the bomb was reevacuated and the

sample pumped under dynamic vacuum until no further release of vapor was detectable using the Baratron gauge. This latter procedure often required extended periods of evacuation (8-16 hours), particularly in the case of PPS powder samples. All subsequent sample handling was carried out under argon in a Vacuum Atmospheres dry box. Doping levels were determined by weight increase and confirmed by elemental analysis (Schwartzkopf Laboratories).

#### *Properties of Poly(p-phenylene Sulfide)*

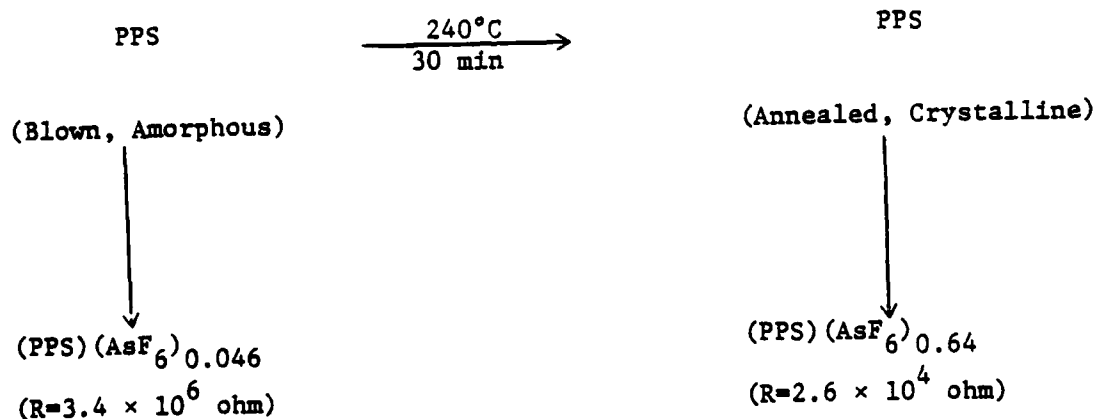
Poly(p-phenylene sulfide) is prepared commercially by the reaction of p-dichlorobenzene with sodium sulfide in a polar solvent.<sup>7,15</sup> The polymer produced by this procedure has a melting point of 285°C and a glass transition temperature of approximately 85°C. PPS is also soluble in solvents such as diphenyl ether at temperatures above 200°C. These properties combine to make PPS a highly processible polymer. To date we have investigated the doping of PPS in the form of powder, biaxially oriented films, blown films, fibers, and monofilament. The film samples were examined with respect to crystallinity by placing them between crossed polarizers under an optical microscope. The blown film showed a dark background characteristic of isotropic amorphous material with the occasional presence of spherulitic structures. In contrast the biaxial film exhibited evidence of orientation as well as a considerable number of spherulites, which lack well defined boundaries since they do not impinge upon one another. As discussed below both the form of the starting polymer and its processing history are found to have a significant effect on the doping process.

PPS is also distinct from other conducting polymer precursors in that its crystal structure is known. Tabor, et al.,<sup>16</sup> have shown that PPS crystallizes with two phenylene sulfide chains passing through the center and edge of an orthorhombic unit cell. Particularly noteworthy is the fact that successive phenylene groups of a given chain alternate at  $\pm 45^\circ$  with respect to the (100) plane. This arrangement minimizes  $\pi$ -overlap along the chain and would at first sight make PPS seem an unlikely prospect for electrical conductivity.

### Doping of PPS

PPS reacts with arsenic pentafluoride to produce a deep blue-black conducting material. The reaction is considerably slower than that of  $\text{AsF}_5$  with polyacetylene<sup>17</sup> and was typically allowed to proceed in a 316 stainless steel reaction vessel for four days at an  $\text{AsF}_5$  pressure of 250 Torr. Under these conditions a limiting composition of approximately  $(\text{PPS})^+(\text{AsF}_6)^-$  is obtained. (Here (PPS) is used to represent the basic polymer repeat unit). The film thickness roughly doubles during the doping process. Although the amount of dopant incorporated may at first seem high, this composition in fact corresponds to 15 mole percent of dopant per carbon atom, a value consistent with the highest reported doping levels for  $\text{AsF}_5$  treated polyacetylene. Lower doping levels may be achieved by appropriate combination of shorter exposure time and lower  $\text{AsF}_5$  pressure.

The rate and extent of doping are particularly sensitive to the degree of crystallinity of the starting polymer. This is best illustrated by the example shown in Equation 1.



Blown PPS is very poorly crystalline as produced. However, annealing at  $240^\circ\text{C}$  for 30 minutes in air produces a highly crystalline film.<sup>7</sup> When a sample of as-received blown film and an annealed sample from the same original sheet were exposed simultaneously to 150 Torr of  $\text{AsF}_5$  for 3.75 days, a dramatic difference in the extent of doping was observed. The final composition of the blown film was  $(\text{PPS})(\text{AsF}_6)_{0.046}$ , whereas the doped annealed film had the composition  $(\text{PPS})(\text{AsF}_6)_{0.64}$ . The

final resistance of the blown film was also two orders of magnitude higher than that of the annealed film, reflecting the different  $\text{AsF}_6$  contents. Thus, the degree of crystallinity seems to be a critical parameter in the doping of PPS. The extent to which crystallinity is important in controlling the rate and extent of doping in other polymer systems is not clear, since in none of the other polymers studied to date can the degree of crystallinity be changed from that obtained in the initial synthesis.

$(\text{PPS})(\text{AsF}_6)_{0.9}$  prepared from 25 micron thick films of biaxially oriented PPS has a flotation density of 1.78 g/cc compared to 1.39 g/cc for the pristine film. The original mechanical properties of the polymer are degraded somewhat by the doping process, the most noticeable change being an increase in brittleness as the doping levels increase. On heating to  $300^\circ\text{C}$  these films slowly lose weight and decrease in conductivity. The DTA and TGA data for a typical sample are shown in Figure 1. Unlike PPS itself these oxidized films do not melt, even on heating to  $900^\circ\text{C}$  by which temperature they appear to have become graphitized.

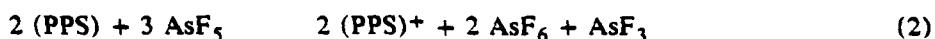
The highest conductivity achieved to date for an  $\text{AsF}_5$  doped biaxially oriented film is  $7 \text{ S-cm}^{-1}$ . For comparison the conductivity of PPS itself is approximately  $10^{-15} \text{ S-cm}^{-1}$  to  $10^{-16} \text{ S-cm}^{-1}$ .<sup>18</sup> The temperature dependence of the conductivity between room temperature and  $175^\circ\text{C}$  is shown in Figure 2 for a typical doped sample. Contact problems have thus far prevented the extension of these measurements to lower temperatures. However, the conductivity is obviously activated in the range explored. Room temperature thermopower measurements confirm that the polymer is p-type ( $S = 50 \mu\text{V-deg}^{-1}$ ) consistent with the expected partial oxidation of the polymer by the  $\text{AsF}_5$ . Both the conductivity and the thermopower of these samples are very sensitive to exposure to the atmosphere; thus all measurements were carried out in a dry box or under argon.

The optical transmission spectra for both lightly and heavily doped 25 micron thick PPS films are shown in Figure 3. Heavily doped PPS samples are blue-black in color; the starting polymer is essentially colorless. The spectrum of a sample of composition  $(\text{PPS})(\text{AsF}_6)_{0.62}$  is shown in Figure 3a and consists primarily of a strong featureless absorption extending through the infrared. This broad absorption is typical of conducting polymers and may be attributed to transitions involving

the free carriers. A less heavily doped dark green  $(\text{PPS})(\text{AsF}_6)_{0.19}$  sample exhibits a prominent feature at 1.75 eV which tails into the infrared (Figure 3b). A very lightly doped  $(\text{PPS})(\text{AsF}_6)_{0.03}$  film is shown in Figure 3d. The absorption at 1.75 eV is now absent and instead a broad peak at 1.1 eV is observed. This 1.1 eV peak in lightly doped PPS is reminiscent of features in the spectra of traditional doped semiconductors which are normally attributed to absorptions due to states introduced into the band gap by the doping process. It is tempting to also attribute the 1.1 eV absorption in lightly doped PPS to states in the gap, with the disappearance of this peak signalling the occurrence of a metal-insulator transition. Such a suggestion must, however, be considered highly speculative at this point, particularly since the nature of the 1.75 eV absorption in somewhat more heavily doped PPS and its relation to the more lightly doped samples is not yet understood.

The situation is complicated by the apparent long-term instability of  $\text{AsF}_5$  treated PPS. The absorption spectrum of the same  $(\text{PPS})(\text{AsF}_6)_{0.19}$  sample after six days under argon in a well maintained dry box is shown in Figure 3c. Although the sample still appeared dark green, the absorption in the infrared has dropped considerably; a new feature (or possibly a previously hidden feature) can be seen at 1.0 eV. Moreover, the peak at 1.75 eV has shifted somewhat to approximately 1.6 eV. These optical changes are accompanied by a decrease in the conductivity of the sample. Although such changes might be attributed to a simple reversal of the doping process, this appears unlikely since one of the reaction products ( $\text{AsF}_3$ ) is pumped off during the doping procedure (see below). Alternatively these changes may reflect a further reaction of the doped polymer; as also discussed below the oxidized PPS, particularly during the early stages of the reaction, may be susceptible to a crosslinking reaction which would effectively return the polymer to a non-conducting state. Since the early stages of doping proceed primarily at the film surface, the changes on standing may also represent some redistribution of the doping to give a more uniform material with a lower local concentration of dopant at the surface. Further experiments currently in progress should allow a better understanding of the long term chemistry of the doping process.

In contrast the chemistry of the initial doping reaction is somewhat better understood. The process is best represented by Equation 2.



Although the precise details of the reaction are not known, the net result is the removal of two electrons from the polymer chain for every three molecules of  $\text{AsF}_5$  reacted. Formal disproportionation of the arsenic species then yields one molecule of  $\text{AsF}_3$  and two molecules of  $\text{AsF}_6$ , the latter serving as counterions to the charge created on the PPS chain. This mechanism is analogous to those previously suggested for the oxidation of both polyacetylene<sup>19</sup> and graphite<sup>20</sup> by  $\text{AsF}_5$ .

The evidence for this mechanism in the case of PPS is quite extensive. Elemental analyses for both undoped PPS and two samples of heavily doped PPS are shown in Table 1. The overall formula is in excellent agreement with that calculated by weight uptake on the assumption that the only arsenic species remaining in the polymer after extensive pumping is the hexafluoroarsenate anion. The arsenic to fluorine ratio is 1:6 for the  $(\text{PPS})(\text{AsF}_6)_{0.59}$  sample and 1:5.9 for the  $(\text{PPS})(\text{AsF}_6)_{0.92}$  sample. The arsenic trifluoride produced according to Equation 2 is a volatile neutral which should be pumped away from the polymer during the preparative procedure.

This hypothesis was confirmed by isolation of the  $\text{AsF}_3$  produced in one doping experiment. In this case the doping with  $\text{AsF}_5$  was allowed to proceed for four days as usual. The bulk of the vapor in the reaction vessel (consisting to a major extent of the large excess of  $\text{AsF}_5$  used in the doping reaction) was quickly pumped off. The sample was then pumped for an additional 5 hours and all volatile material evolved during this period was collected in a liquid nitrogen trap. After fractionation to remove the very low boiling  $\text{AsF}_5$  fraction, the residue was subjected to mass spectroscopic analysis and found to be essentially pure  $\text{AsF}_3$ .<sup>21</sup> The amount of  $\text{AsF}_3$  collected in this procedure corresponded to approximately 20% that expected on the basis of Equation 2. No quantitative estimate was made of the amount of  $\text{AsF}_3$  discarded in the initial  $\text{AsF}_5$  rich fraction.

The identification of the arsenic containing species remaining in the doped PPS as  $\text{AsF}_6$  can be confirmed spectroscopically. The infrared spectra in transmission of both a lightly doped 25 micron thick film and a heavily doped very thin film (prepared from the melt) are shown in Figure 4. In addition to peaks arising from both unreacted and doped polymer chains, a peak can be seen at  $705\text{--}710\text{ cm}^{-1}$  corresponding to the characteristic absorption of the hexafluoroarsenate anion.<sup>18</sup> The X-ray absorption spectrum of heavily doped PPS also shows an arsenic K-shell pre-absorption edge shift typical of  $\text{AsF}_6$  as a small shoulder located 6.7 eV below the main absorption.<sup>22</sup>

X-ray powder pattern data demonstrate the drastic reduction in the PPS crystallinity on doping. Figure 5 shows the X-ray spectra of crystalline PPS before and after doping. The spectrum of amorphous blown PPS is also included for comparison. As can be seen the spectra of amorphous and doped PPS are quite similar, indicative of the extensive disorder introduced in the doping process. This effect, of course, makes it impossible to determine the nature of the intercalation of the dopant species between the PPS chains, if, indeed, intercalation can be considered a useful model in this system.

As is often the case in these materials, the nature of the changes caused in the polymer chain by the doping process are difficult to understand spectroscopically. Infrared spectra of a blown film before and after annealing (which is known to increase crystallinity as discussed above) reveal a number of bands whose intensity is sensitive to the crystalline content of the polymer. The intensities of the absorptions at  $482$ ,  $560$ ,  $1097$ , and  $1900\text{ cm}^{-1}$  are observed to increase considerably on annealing, while those at  $1080$  and  $1575\text{ cm}^{-1}$  diminish in intensity. A strong band at  $810\text{ cm}^{-1}$  is also observed to shift to  $822\text{ cm}^{-1}$  after annealing. Interestingly, on doping PPS films with  $\text{AsF}_5$  a number of bands are observed to undergo dramatic intensity changes. These intensity variations correlate very well with those observed in the annealing experiments and indicate a considerable decrease in the crystalline content of the films on doping, as previously suggested by the X-ray measurements discussed above.

The infrared spectrum of a lightly doped (PPS)(AsF<sub>6</sub>)<sub>0.169</sub> film shows new bands characteristic of the doped polymer at 1547, 1048, 1035, 996, and 887 cm<sup>-1</sup> (Figure 4). As in the case of polyacetylene<sup>23</sup> the free carrier absorption in the infrared is sufficiently intense that transmission spectra of heavily doped-free standing PPS films can not be obtained. Instead thin films of PPS were prepared from the melt on cesium iodide substrates and then exposed to AsF<sub>5</sub>. As can be seen in Figure 4 features at 1326, 1310, 1270, 1112, and 700 cm<sup>-1</sup> are observed in addition to the bands observed in the lightly doped sample. The peculiar shape of the bands in the heavily doped film attributable to residual pristine PPS is due to the granular texture of the polymer after melt crystallization on the CsI support. This scattering is commonly referred to as the Christiansen effect<sup>24</sup> and is absent in commercial films which are prepared under pressure, a procedure which causes the polymer to flow and removes the granular texture. The intensity of the AsF<sub>6</sub> band at 705-710 cm<sup>-1</sup> contains a sizable contribution from the reaction of CsI with AsF<sub>5</sub> as observed previously.<sup>23</sup>

Raman spectra of pristine and doped PPS resin are shown in Figure 6. Part of the apparent band broadening observed in the doped sample is instrumental in origin and results from the larger slit widths (8 cm<sup>-1</sup> resolution) used to record the spectrum. In contrast the pristine PPS spectrum was recorded at a resolution of 3 cm<sup>-1</sup>. There is also, however, an additional contribution to the bandwidth which results from the structural disorder introduced by the doping process. New peaks attributable to the doped polymer are observed at 1596, 1589, 1287-1314, 1086, and 536 cm<sup>-1</sup>. Weaker bands in the 1420-1520, 1150-1250, and 700-750 cm<sup>-1</sup> are also in evidence.

With one exception,<sup>25</sup> little data is currently available on the assignment of the infrared and Raman fundamentals in PPS. Many of the observed bands can be assigned to localized vibrations of the phenyl ring while a few others are attributed to motions of the phenyl-sulfur group<sup>25,26</sup>. Those which show the greatest change on doping occur in the 1500-1600 and 1300-1400 cm<sup>-1</sup> regions in both the infrared and Raman spectra. The former region contains bands which are assigned to the C-C stretching modes of the phenyl ring;<sup>25,26</sup> after doping new bands appear at 1547 (IR) and 1596 cm<sup>-1</sup> (Raman). This suggests some alteration of the electronic structure of the phenyl ring which may

arise from a branching or crosslinking mechanism<sup>27</sup> resulting in the presence of tri-substituted phenyl rings. The nature of the strong Raman triplet at 1314, 1304, and 1287  $\text{cm}^{-1}$  is more elusive and may involve motions of the oxidized sulfur group in the doped polymer. It is clear that this broad triplet is a new band which persists even when the  $\text{AsF}_5$  doped PPS is exposed to air for an extended period of time.

The strong Raman band at 1073  $\text{cm}^{-1}$  in pristine PPS characteristic of an aromatic-sulfur stretching vibration<sup>28</sup> broadens on doping with a decrease in intensity and a shift of 13  $\text{cm}^{-1}$  to higher frequency. The nature of this behavior and the origin of the IR band at 1038  $\text{cm}^{-1}$  are not yet clear and are the subjects of work currently in progress.<sup>29</sup>

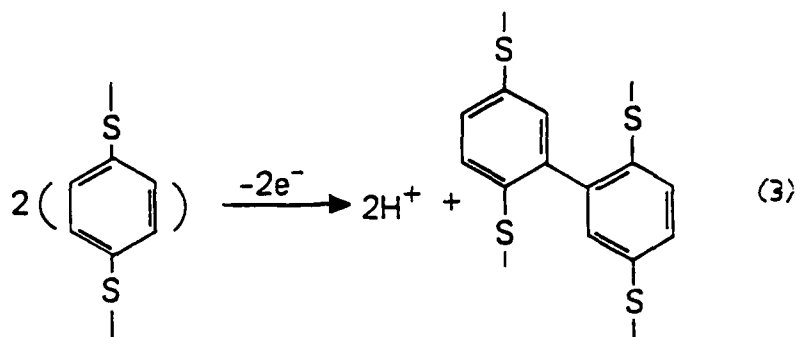
The appearance of a band of moderate strength at 536  $\text{cm}^{-1}$  in the Raman spectrum of doped PPS is suggestive of disulfide linkages, which may result from some sort of crosslinking or chain scission on exposure to  $\text{AsF}_5$ . This would involve considerable loss of crystallinity and is consistent with the IR intensity measurements and X-ray diffraction data presented above.

The spectroscopic information obtained to date sheds no light on the fundamental question of how electrical conductivity can be achieved along a polymer chain in which the neighboring phenylene groups are initially almost orthogonal. Several possible explanations may be considered. The most trivial possibility is that the doping process somehow allows the phenylene groups to rotate into a conformation allowing better  $\pi$ -overlap along the chain. Why this should occur is not clear.

An intriguing alternate possibility is that the electronic overlap is transmitted along the chain through the sulfur d-orbitals in such a way that successive phenylene groups need not be coplanar for effective conjugation. In this respect it is interesting to note that poly(p-phenylene oxide) (PPO) cannot be doped to high levels of conductivity with  $\text{AsF}_5$ , although this material does react with  $\text{AsF}_5$  to give an unidentified black product (see below). PPO is known to have a crystal structure very like that of PPS;<sup>6</sup> thus it is tempting to attribute the difference in results to the lack of low lying d-orbitals in the oxygen derivative. This argument is complicated, however, by the known greater ease of

oxidation of organosulfur compounds compared to their oxygen analogs.<sup>30</sup> It may be that PPO is sufficiently difficult to oxidize compared to PPS that a different chemical reaction intervenes.

A final possibility is that on doping the PPS undergoes other chemistry in addition to the oxidation reaction described above. In particular, the solution phase electrochemistry of donor substituted aromatics suggests that oxidative coupling of the phenylene rings should be a facile process (Equation 3).<sup>31</sup>



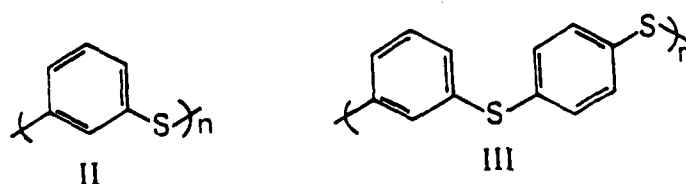
In PPS this would lead to crosslinking and conjugative overlap perpendicular to the original chain direction. In support of this hypothesis it may be noted that the elemental analysis results in Table 1 show that doped PPS is somewhat hydrogen deficient compared to PPS itself; the data also suggest that the hydrogen deficiency increases as the doping level is raised. Moreover, although PPS may be stretched to draw ratios greater than 10, the electrical conductivity of these samples on doping shows negligible anisotropy. This could arise from the introduction of crosslinks, but it may also be simply a manifestation of the destruction of the PPS crystallinity during the doping process.

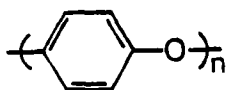
We have examined other potential dopants in the hope of finding an oxidizing (or reducing) agent which generates a more conducting or more ordered product than does  $\text{AsF}_5$ . Iodine and bromine prove insufficiently strong oxidizing agents to remove electrons from PPS. The exposure of PPS to  $\text{SO}_3$  initially enhances the sample conductivity somewhat, but a rapid degradation of the polymer ensues. Sodium naphthalide in THF also leads to rapid degradation of the PPS.<sup>32</sup> As has been observed in other conducting polymers, the treatment of  $\text{AsF}_5$  doped PPS with ammonia rapidly reduces the sample conductivity. Although this has been described as a compensation process, the actual mechanism of reaction is not clear at this point.

Quite interesting results were obtained in an attempt to electrochemically oxidize a thin film of PPS prepared from the melt on a gold electrode. The cyclic voltammogram for this sample in acetonitrile with tetrabutylammonium perchlorate as the supporting electrolyte is shown in Figure 7. A partially reversible oxidation is observed at approximately 1.35 V (vs. SCE), somewhat higher than the value of 1.19 V reported for 1,4-bis(methylthio)benzene<sup>30b</sup>. For the reversible oxidation of a material on an electrode surface, the forward and reverse waves are expected to occur at the same potential. This is clearly not the case for PPS; moreover the inequality of the areas under the forward and reverse waves also indicates a non-reversible process. The sample was subsequently stepped to 1.5 V and allowed to sit at this potential for several minutes. Although the number of coulombs passed suggests that as much as 20% of the PPS was oxidized under these conditions, no color change was observed in the polymer film nor did the film become conducting. This implies that the electrochemical oxidation involves a somewhat different chemical reaction than the oxidation by  $\text{AsF}_5$ . One intriguing possibility is that the electrochemically induced reaction produces radical cations which couple as shown in Equation 3 to form crosslinked polymer, but that this material does not undergo further oxidation at the potentials examined.

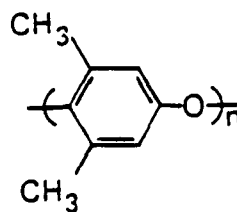
#### *Derivatives of PPS*

Several derivatives of PPS have also been investigated as potential conducting polymer precursors. Poly(m-phenylene sulfide) (II) and the random copolymer poly(m,p-phenylene sulfide) (III) can both be doped with  $\text{AsF}_5$  to give black materials with conductivities comparable to that of doped PPS.

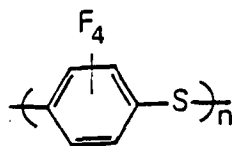




IV



V



VI

As noted above poly(p-phenylene oxide) (IV) reacts with  $\text{AsF}_5$  to give a black solid, but high levels of conductivity are not obtained. Treatment of commercially available poly(2,6-dimethyl-p-phenylene oxide) (V) with  $\text{AsF}_5$  produces results similar to those obtained with (IV). Low molecular weight oligomers of poly(tetrafluoro-p-phenylene sulfide) (VI) showed no reactivity toward  $\text{AsF}_5$ ; as anticipated the strongly electron withdrawing fluorine substituents cause this derivative to be significantly more difficult to oxidize than PPS. More disappointing, however, is the observation that reaction of VI with sodium naphthalide leads only to degradation. No indication of the generation of the desired n-type material was obtained.

#### *Acknowledgments*

We thank the Office of Naval Research for partial support of this work.

## REFERENCES

1. For reviews see G. B. Street and T. C. Clarke, ACS Adv. in Chemistry, **186**, in press; G. B. Street and T. C. Clarke, IBM J. Res. Dev., in press.
2. R. L. Greene, G. B. Street, and L. J. Suter, Phys. Rev. Lett., **34**, 577 (1975).
3. (a) C. K. Chiang, C. R. Fincher, Jr., Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau, and A. G. MacDiarmid, Phys. Rev. Lett., **39**, 1098 (1977).  
(b) A. G. MacDiarmid and A. J. Heeger, Synthetic Metals, **1**, 101 (1980).
4. (a) A. F. Diaz, K. K. Kanazawa, and G. P. Gardini, JCS Chem. Commun., 635 (1979).  
(b) K. K. Kanazawa, A. F. Diaz, R. H. Geiss, W. D. Gill, J. F. Kwak, J. A. Logan, J. F. Rabolt, and G. B. Street, JCS Chem. Commun., 854 (1979).  
(c) K. K. Kanazawa, A. F. Diaz, G. P. Gardini, W. D. Gill, P. M. Grant, J. F. Kwak, and G. B. Street, Synthetic Metals, **1**, 329 (1980).
5. (a) D. M. Ivory, G. G. Miller, J. M. Sowa, L. W. Shacklette, R. R. Chance, and R. H. Baughman, J. Chem. Phys., **71**, 1506 (1979).  
(b) L. W. Shacklette, R. R. Chance, D. M. Ivory, G. G. Miller, and R. H. Baughman, Synthetic Metals, **1**, 307 (1980).
6. J. Boon and E. P. Magre, Makromolec. Chem., **126**, 130 (1969).
7. See D. G. Brady, J. Appl. Polym. Sci., **20**, 2541 (1976) for leading references.
8. A preliminary report of this work has appeared: J. F. Rabolt, T. C. Clarke, K. K. Kanazawa, J. R. Reynolds, and G. B. Street, JCS Chem. Commun., 347 (1980).

9. Similar results have been reported independently: R. R. Chance, L. W. Shacklette, G. G. Miller, D. M. Ivory, J. M. Sowa, R. L. Elsenbaumer, and R. H. Baughman, *JCS Chem. Commun.*, 348 (1980).
10. I. Haddad, S. Hurley, and C. S. Marvel, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 2793 (1973).
11. We thank R. Balanson for samples of this polymer.
12. We thank W. Volksen for a sample of this material.
13. (a) P. Robson, M. Stacey, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 4754 (1960).  
(b) E. V. Aroskar, M. D. Chaudhry, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 2975 (1964).
14. D. R. Stull, *Ind. Eng. Chem.*, **39**, 540 (1947).
15. J. T. Edmonds, Jr., and H. W. Hill, Jr., U. S. Patent 3,354,129 (November 21, 1967).
16. B. J. Tabor, E. P. Magre, and J. Boon, *Eur. Polym. J.*, **7**, 1127 (1971).
17. cf. T. C. Clarke, R. H. Geiss, W. D. Gill, P. M. Grant, H. Morawitz, G. B. Street, and D. E. Sayers, *Synthetic Metals*, **1**, 21 (1979).
18. Technical Service Memorandum TSM-266, Phillips Petroleum Co., Bartlesville, Okla.
19. T. C. Clarke and G. B. Street, *Synthetic Metals*, **1**, 119 (1980).
20. (a) N. Bartlett, R. N. Biagioni, B. W. McQuillan, A. S. Robertson, and A. C. Thompson, *JCS Chem. Commun.*, 200 (1978).  
(b) N. Bartlett, B. McQuillan, and A. S. Robertson, *Mater. Res. Bull.*, **13**, 1259 (1978).
21. T. Inoue, J.-E. Osterholm, H. K. Yasuda, and L. L. Levenson, *Appl. Phys. Lett.*, **36**, 101 (1980).

22. H. Morawitz, P. M. Grant, and D. E. Sayers, unpublished results.
23. J. F. Rabolt, T. C. Clarke, and G. B. Street, *J. Chem. Phys.*, **71**, 4614 (1979).
24. W. J. Potts, Jr., *Chemical Infrared Spectroscopy*, Wiley, 1963.
25. J. F. Rabolt, Ph. D. Thesis, Southern Illinois University, 1974.
26. D. H. Whiffen, *J. Chem. Soc.*, 1350 (1956).
27. R. T. Hawkins, *Macromolecules*, **9**, 189 (1976).
28. D. A. Long, *Raman Spectroscopy*, McGraw-Hill, 1977.
29. J. F. Rabolt, T. C. Clarke, and G. B. Street, to be published.
30. (a) A. Zweig, W. G. Hodgson, and W. H. Jura, *J. Am. Chem. Soc.*, **86**, 4124 (1964).  
(b) A. Zweig and J. E. Lehnson, *J. Am. Chem. Soc.*, **87**, 2647 (1965).
31. H. G. H. Erdtman, *Proc. Roy. Soc. (London)*, **A143**, 191 (1934).
32. Alkali metal vapors have been reported to successfully dope PPS to give an n-type material.<sup>9</sup>

Table 1. Results of Elemental Analysis for Pristine and AsF<sub>5</sub> Doped PPS.

Sample	C	H	S	As	F	Total	Formula by Analysis <sup>a</sup>
(PPS) <sup>b</sup>	66.29	3.89	29.02			99.20	C <sub>6</sub> H <sub>4.22</sub> S <sub>0.98</sub>
(PPS) <sup>c</sup>	66.47	3.78	29.32			99.57	C <sub>6</sub> H <sub>4.09</sub> S <sub>0.98</sub>
(PPS)(AsF <sub>6</sub> ) <sub>0.59</sub> <sup>d</sup>	33.00	1.30	14.40	20.40	31.00	100.10	C <sub>6</sub> H <sub>2.48</sub> S <sub>0.98</sub> (AsF <sub>6.08</sub> ) <sub>0.59</sub>
(PPS)(AsF <sub>6</sub> ) <sub>0.92</sub> <sup>d</sup>	27.26	0.74	10.58	24.53	36.56	99.67	C <sub>6</sub> H <sub>1.45</sub> S <sub>0.87</sub> (AsF <sub>5.91</sub> ) <sub>0.86</sub>

(a) Empirical formula calculated from elemental analysis data; normalized to six carbons per repeat unit.

(b) PPS powder, undoped.

(c) Biaxially oriented PPS film, undoped.

(d) AsF<sub>5</sub> doped biaxially oriented PPS film; approximate stoichiometry determined by weight uptake.

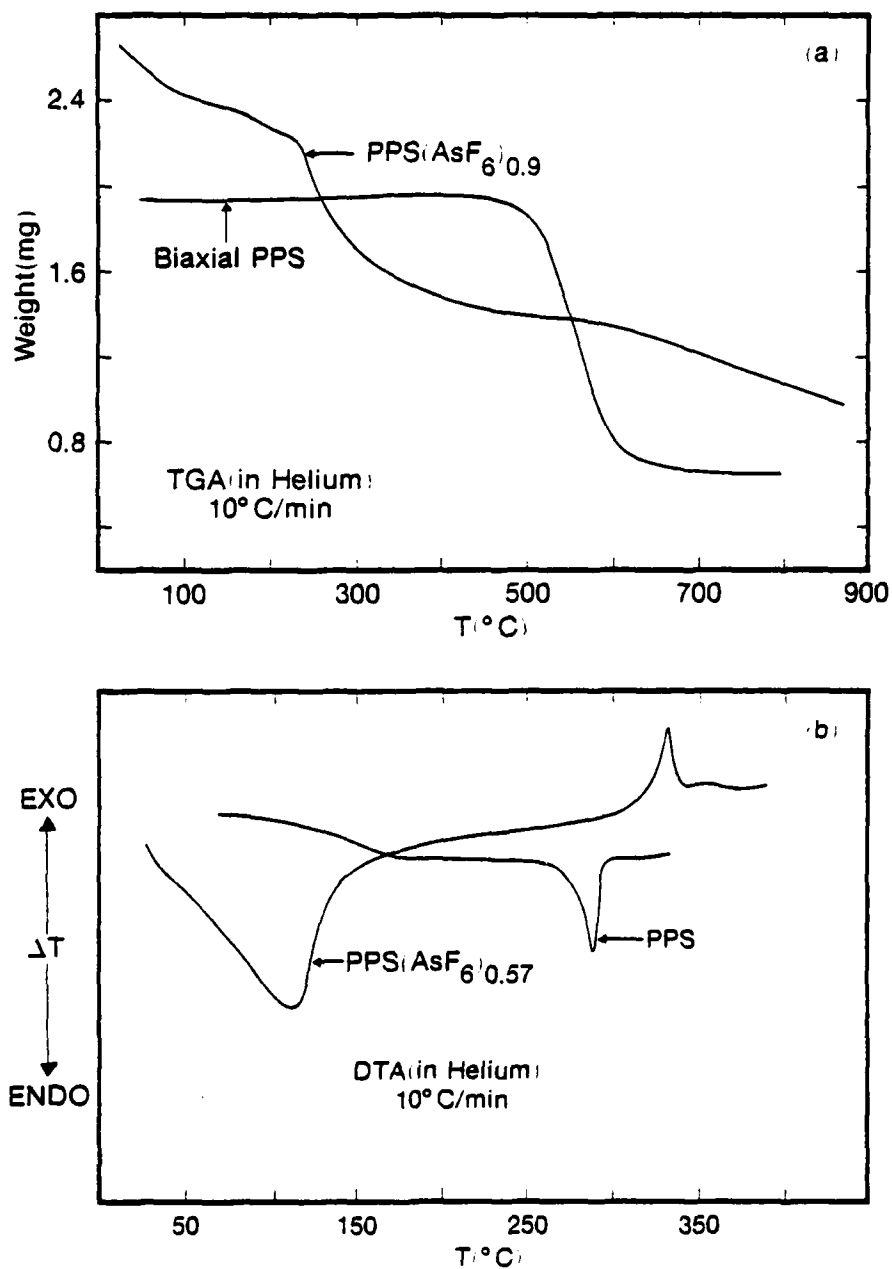


Figure 1. (a) Thermogravimetric analysis of PPS and  $\text{PPS}(\text{AsF}_6)_{0.57}$ . (b) Differential thermal analysis of PPS and  $\text{PPS}(\text{AsF}_6)_{0.9}$ .

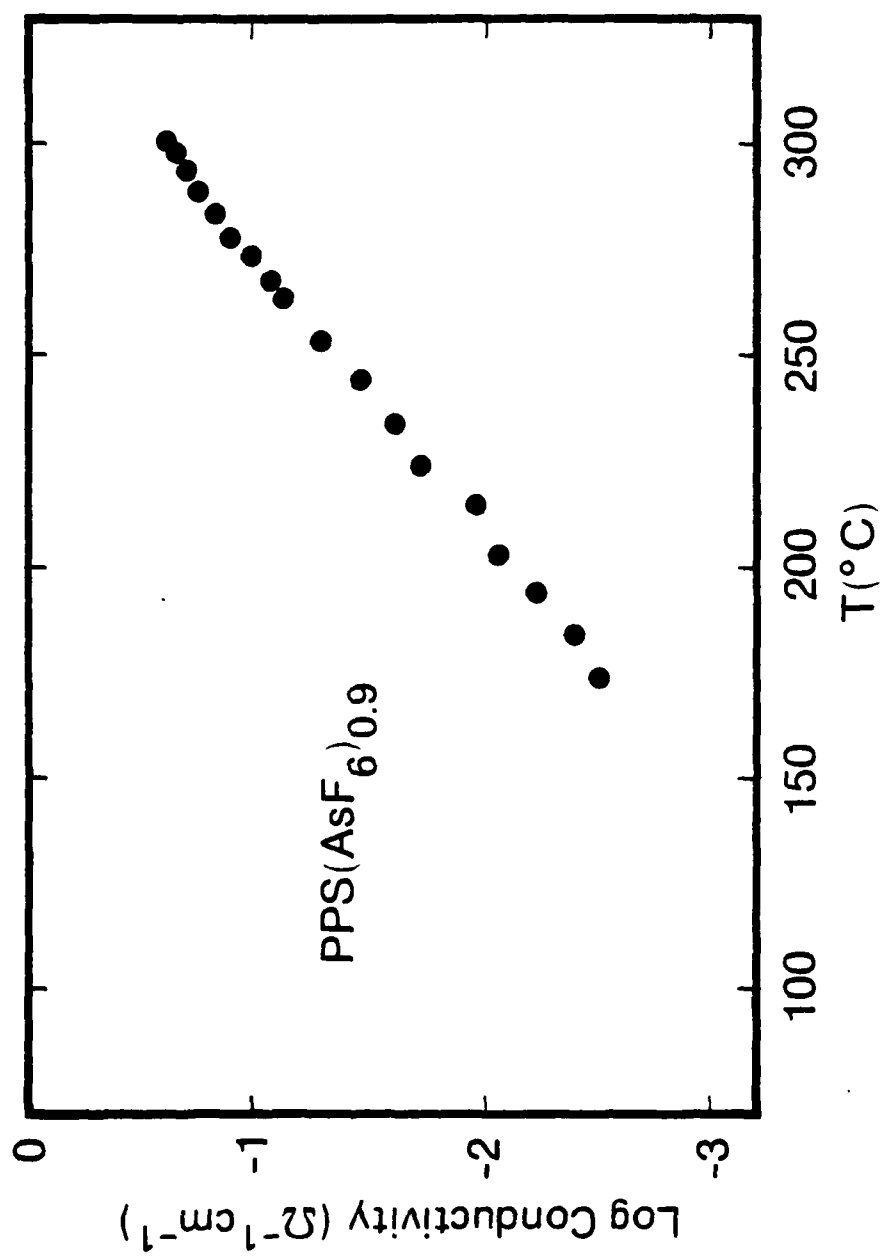


Figure 2. Temperature dependence of the conductivity of PPS(AsF<sub>6</sub>)<sub>0.9</sub>.

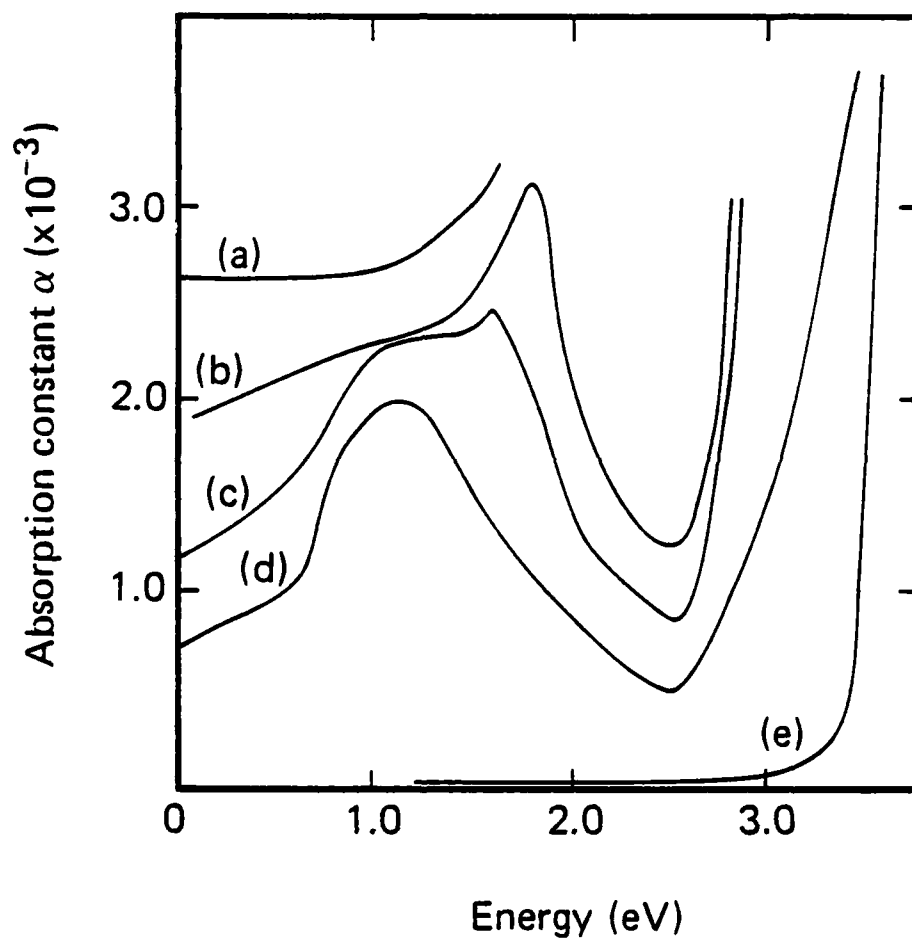


Figure 3.

Absorption constant as a function of energy for (a)  $(\text{PPS})(\text{AsF}_6)_{0.62}$ ; (b)  $(\text{PPS})(\text{AsF}_6)_{0.19}$ ; (c)  $(\text{PPS})(\text{AsF}_6)_{0.19}$  after aging for six days in dry box; (d)  $(\text{PPS})(\text{AsF}_6)_{0.03}$ ; (e) pristine PPS.

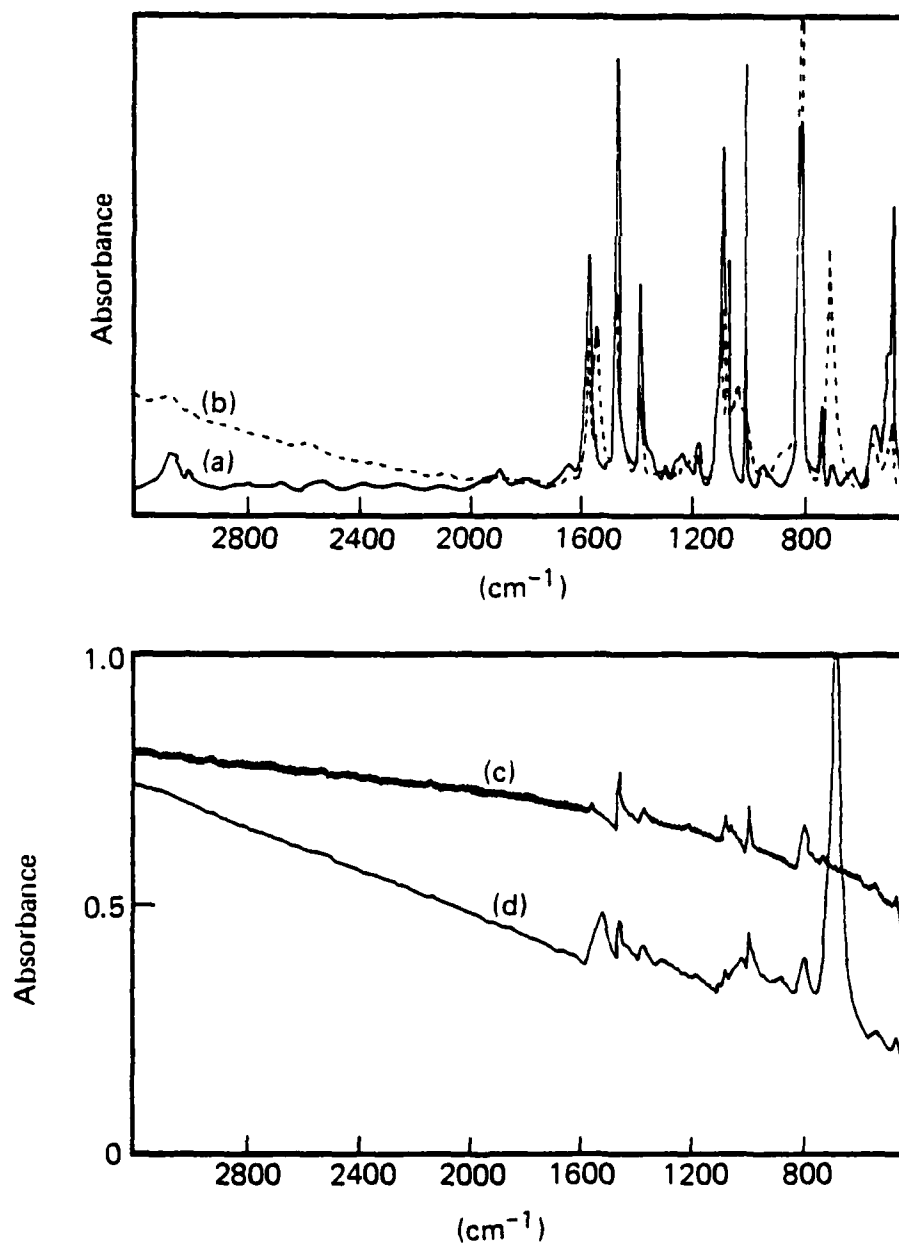


Figure 4. Infrared spectra of undoped and  $\text{AsF}_5$  treated PPS: (a) pristine blown PPS film; (b)  $(\text{PPS})(\text{AsF}_6)_{0.169}$  prepared from blown PPS film; (c) thin PPS film prepared from the melt on CsI; (d) heavily  $\text{AsF}_5$  doped thin PPS film on CsI.

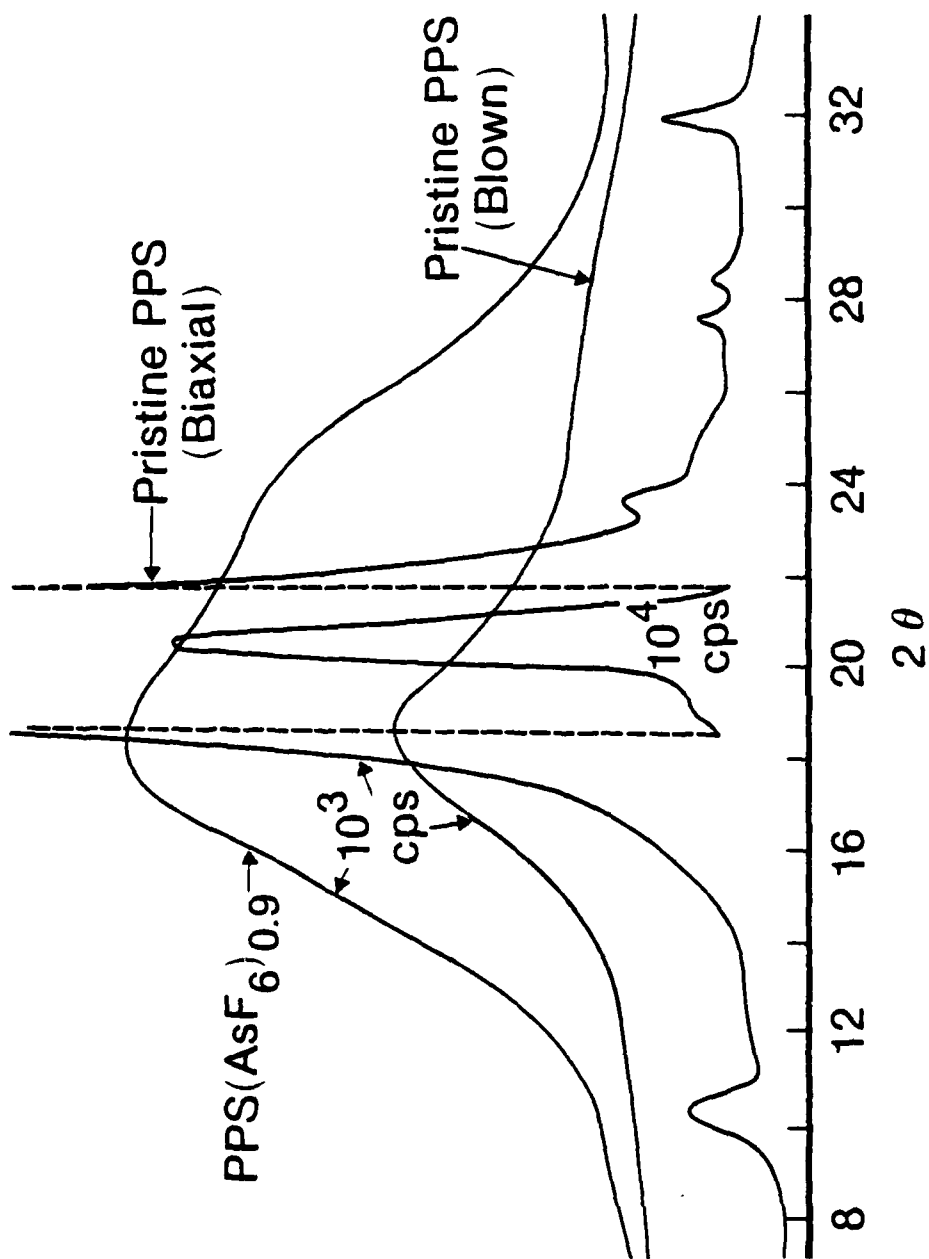


Figure 5. X-ray diffraction data for (a) pristine PPS (biaxially oriented); (b) pristine PPS (blown); (c) PPS(AsF<sub>6</sub>)<sub>0.9</sub>.

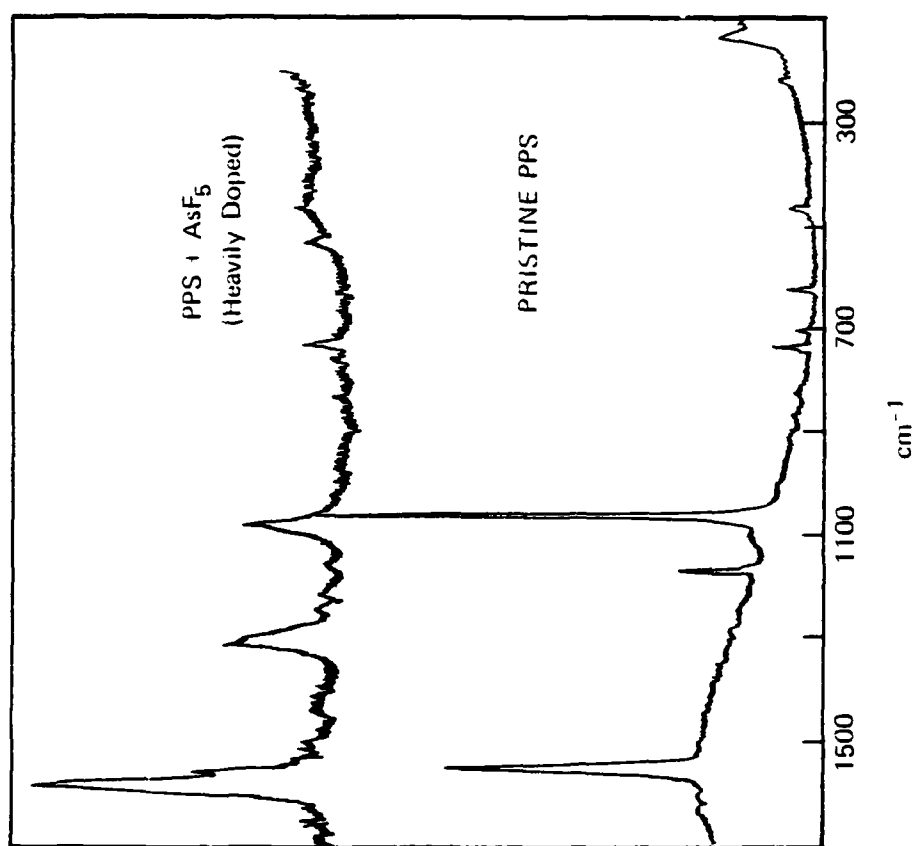


Figure 6. Raman spectra of PPS before ( $\lambda = 457.9 \text{ nm}$ ,  $3 \text{ cm}^{-1}$  bandpass, spinning cell) and after ( $\lambda = 457.9$ ,  $8 \text{ cm}^{-1}$  bandpass, sealed capillary spinning cell) doping with  $\text{AsF}_5$ .

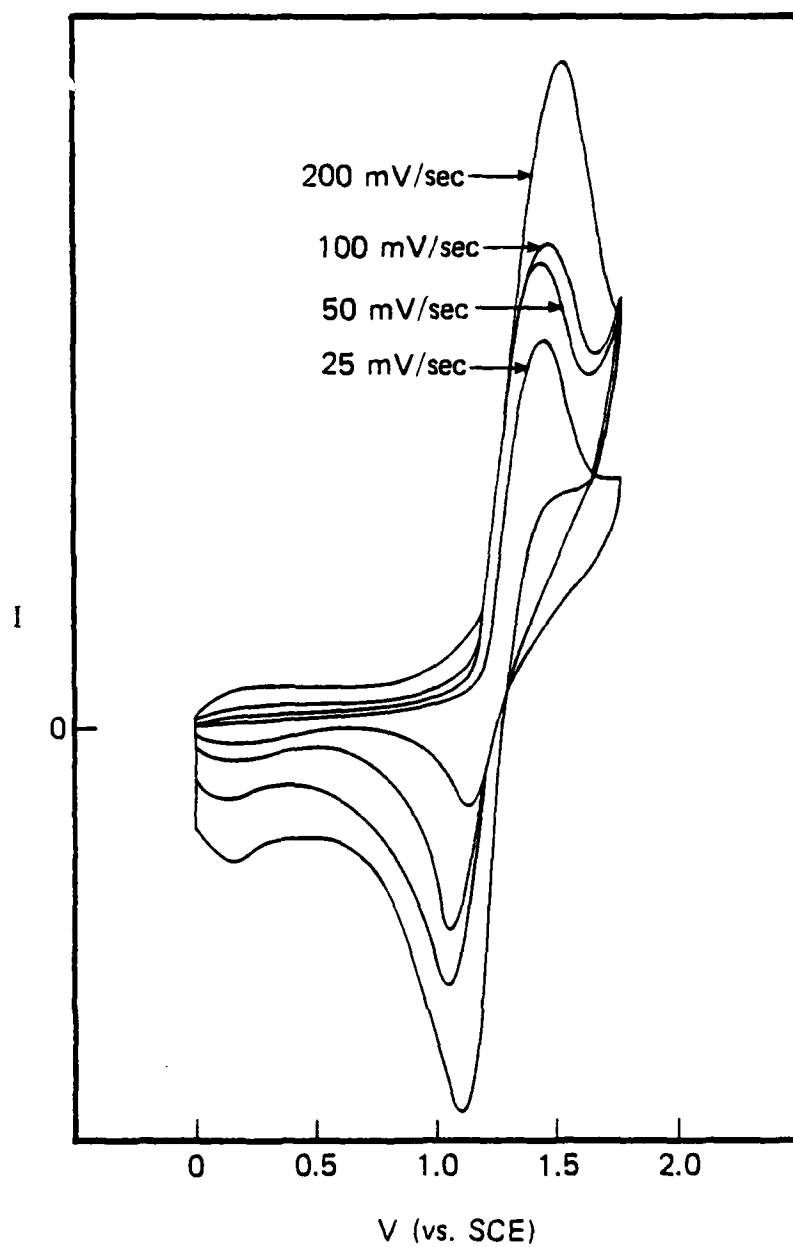


Figure 7. Cyclic voltammogram of PPS film on gold electrode in acetonitrile.

**DAT  
ILM**